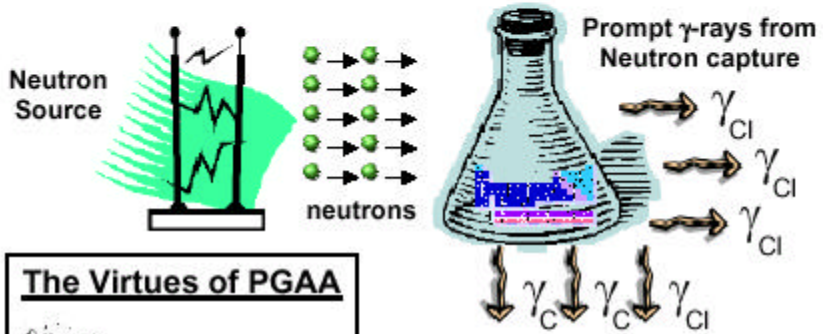
Analysis of Unknown Materials with Prompt Gamma-ray Activation Analysis (PGAA)



The Virtues of PGAA

- Nondestructive
- Simultaneous
- *In situ*
- Quantitative
- Prompt
- Minimizes waste
- Maximizes safety

Ge γ-ray Detector & Sample Holder

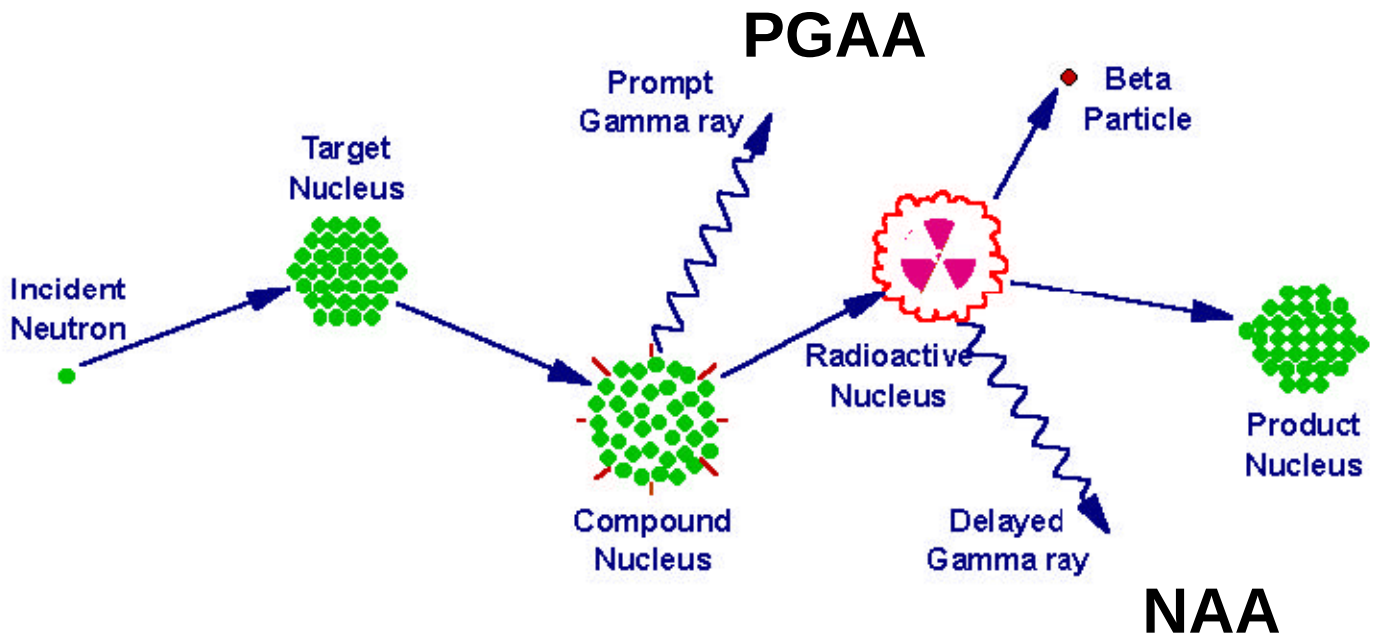
Analysis of all elements

Computer

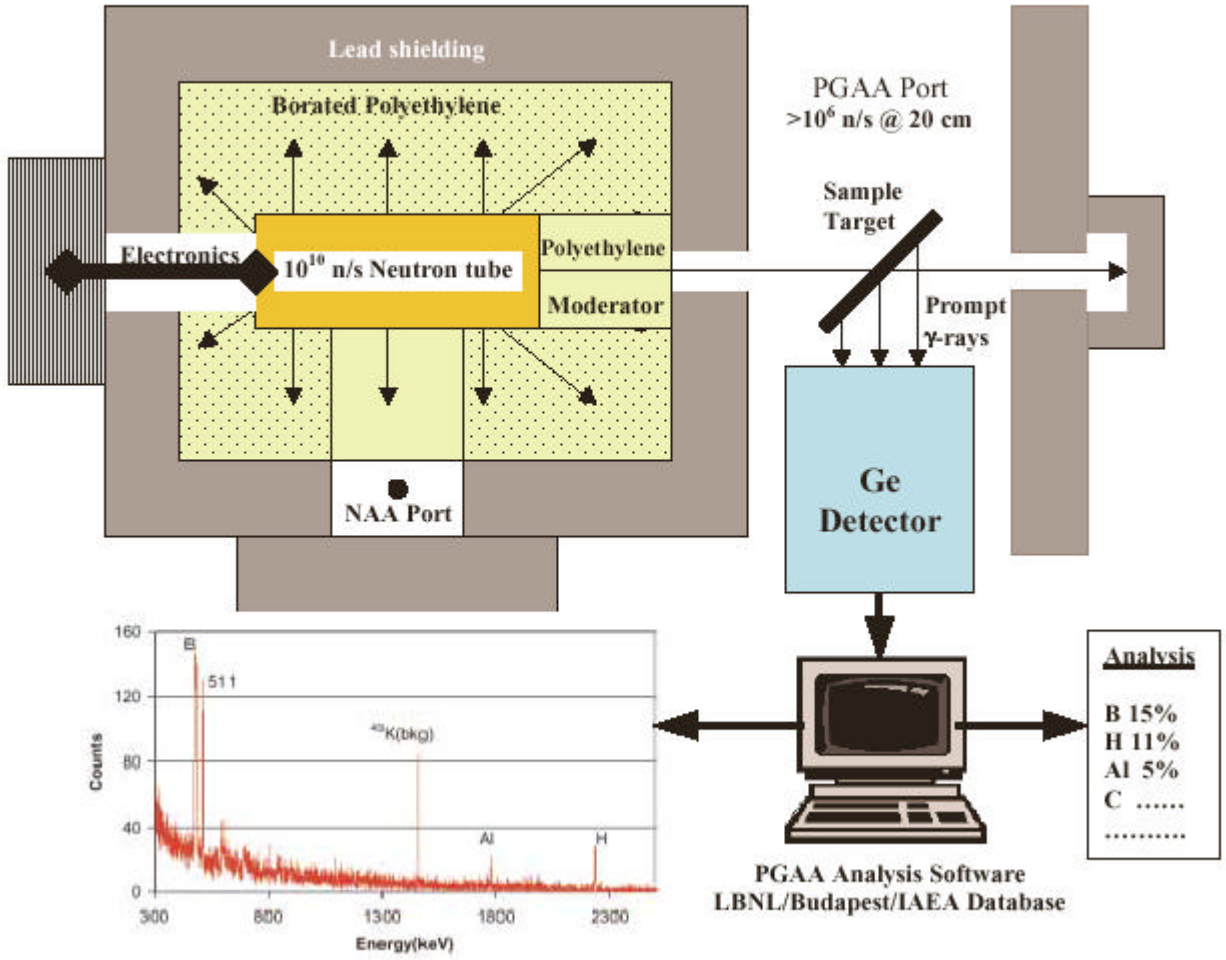
Database

CCl_4

Prompt Gamma-Ray Activation Analysis Method



Portable PGAA/NAA Analysis System



Advantages of the PGAA Method

- **Nondestructive** analysis preserves samples for further analysis
- **Simultaneous** analysis of all elements (isotopes) from Hydrogen to Uranium and beyond
- **Uniform** sample analysis
- ***In situ*** analysis requiring no sample preparation
- **Quantitative** analysis of all major components of a sample (mg to ppb sensitivity depending on the element)

Requirements for PGAA

Gamma Ray Detection System

- **Compton Suppressed Ge –** or cluster Ge detectors
- **High Resolution 0 – 11 MeV**
- **Shielding –** from background and gammas from scattered neutrons
- **Fission detectors –** analysis of fissionable actinides
- **Analysis Software –** developed at Budapest Reactor

PGAA Sensitivity

For a system with 10^6 n/sec, the detection limit per cm^3 *

- – B, Cd, Sm, Eu, Gd
- – H, Cl, Sc, Mn, Co, Se, Kr, Rh, In, Xe, Cs, Nd, Dy, Er, Yb, Re, Au, Hg
- – Na, K, Ti, V, Cr, Fe, Ni, Cu, As, Mo, Ru, Pd, Ag, Te, I, La, Pr, Tb, Ho, Tm, Lu, Hf, W, Os, Ir, Pt, Th
- – Li, N, Ne, Mg, Al, Si, P, S, Ar, Ca, Zn, Ga, Ge, Br, Rb, Sr, Zr, Nb, Sn, Sb, Ba, Ce, Tl
- – Be, C, O, F,Y, Ta, Pb, Bi He

* From C. Yonezawa, Analytical Science 2, 303 (1994))

PGAA Elemental Sensitivity

1 H 1.00794 0.333 b 20.5 b																	2 He 4.002602 3.10E-05 b 3.10 b
3 Li 6.941 0.0449 b 0.95 b	4 Be 9.012182 0.0076 b 6.2 b											5 B 10.811 764 b 4.32 b	6 C 12.0107 0.00351 b 4.74 b	7 N 14.00674 0.075 b 10.0 b	8 O 15.9994 1.90E-04 b 3.75 b	9 F 18.9984032 0.0096 b 3.64 b	10 Ne 20.1797 0.0395 b 2.41 b
11 Na 22.989770 0.400 b 3.03 b	12 Mg 24.3050 0.063 b 3.27 b											13 Al 26.981538 0.231 b 1.41 b	14 Si 28.0855 0.171 b 1.91 b	15 P 30.973761 0.172 b 3.13 b	16 S 32.066 0.52 b 0.92 b	17 Cl 35.4527 33.1 b 15.9 b	18 Ar 39.948 0.68 b 0.249 b
19 K 39.0983 2.06 b	20 Ca 40.078 0.431 b 2.93 b	21 Sc 44.955910 9.8 b 22.4 b	22 Ti 47.867 6.1 b 3.71 b	23 V 50.9415 4.89 b 4.81 b	24 Cr 51.9961 3.07 b 3.28 b	25 Mn 54.938049 13.3 b 2.20 b	26 Fe 55.845 2.56 b 11.6 b	27 Co 58.933200 20.4 b 6.0 b	28 Ni 58.6934 4.46 b 17.9 b	29 Cu 63.546 3.78 b 7.9 b	30 Zn 65.39 0.90 b 4.28 b	31 Ga 69.723 1.07 b	32 Ge 72.61 0.79 b 4.06 b	33 As 74.92160 4.50 b 5.4 b	34 Se 78.96 15.3 b 9.0 b	35 Br 79.904 1.35 b	36 Kr 83.80 22.5 b
37 Rb 85.4678 0.342 b	38 Sr 87.62 1.25 b	39 Y 88.90585 0.00100 b 7.7 b	40 Zr 91.224 0.192 b 5.2 b	41 Nb 92.90638 1.15 b 6.4 b	42 Mo 95.94 2.57 b	43 Tc [98]	44 Ru 101.07 2.57 b	45 Rh 102.90550 145 b	46 Pd 106.42 7.4 b 2.51 b	47 Ag 107.8682 2.43 b 5.09 b	48 Cd 112.411 2520 b 2.17 b	49 In 114.818 156 b 2.65 b	50 Sn 118.710 0.63 b 3.37 b	51 Sb 121.760 1.78 b	52 Te 127.60 4.53 b 0.183 b	53 I 126.90447 6.2 b	54 Xe 131.29 23.8 b
55 Cs 132.90545 29.0 b	56 Ba 137.327 0.84 b	57 La 138.9055 9.0 b 10.1 b	72 Hf 178.49 29.7 b 10.3 b	73 Ta 180.9479 0.079 b 6.1 b	74 W 183.84 17.8 b 4.96 b	75 Re 186.207 43.6 b 11.4 b	76 Os 190.23 10.9 b 8.2 b	77 Ir 192.217 3.70 b 5.6 b	78 Pt 195.078 9.6 b 11.8 b	79 Au 196.96655 99 b 7.8 b	80 Hg 200.59 384 b 11.1 b	81 Tl 204.3833 3.44 b 10.0 b	82 Pb 207.2 0.168 b	83 Bi 208.98038 0.0096 b 9.3 b	84 Po [209]	85 At [210]	86 Rn [222]
87 Fr [223]	88 Ra [226]	89 Ac [227]	104 Rf [261]	105 Db [262]	106 Sg [266]	107 Bh [264]	108 Hs [269]	109 Mt [268]	110 [271]	111 [272]	112 [277]	113	114	115	116	117	118

58 Ce 140.116 1.78 b 2.50 b	59 Pr 140.90765 11.5 b 2.54 b	60 Nd 144.24 49.5 b 14.1 b	61 Pm [145]	62 Sm 150.36 5613 b 30.5 b	63 Eu 151.964 2983 b 8.1 b	64 Gd 157.25 48770 b 165 b	65 Tb 158.92534 23.4 b 6.9 b	66 Dy 162.50 488 b 94 b	67 Ho 164.93032 3.50 b 8.6 b	68 Er 167.26 158 b 9.0 b	69 Tm 168.93421 8.2 b 6.3 b	70 Yb 173.04 35.7 b 18.6 b	71 Lu 174.967 24.0 b 7.0 b
90 Th 232.0381 7.4 b	91 Pa 231.03588	92 U 238.0289 3.37 b 9.4 b	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [262]

Z Element

atomic weight

σ(capture)

σ(scattering)

Detection Limit*

- <10 ng
- <1 ug
- <10 ug
- <100 ug
- >100 ug
- No data

* Per cm^3 based on 0.01 captures per second assuming 10^6 neutrons/cm^2 and neglecting gamma-ray detection efficiency.

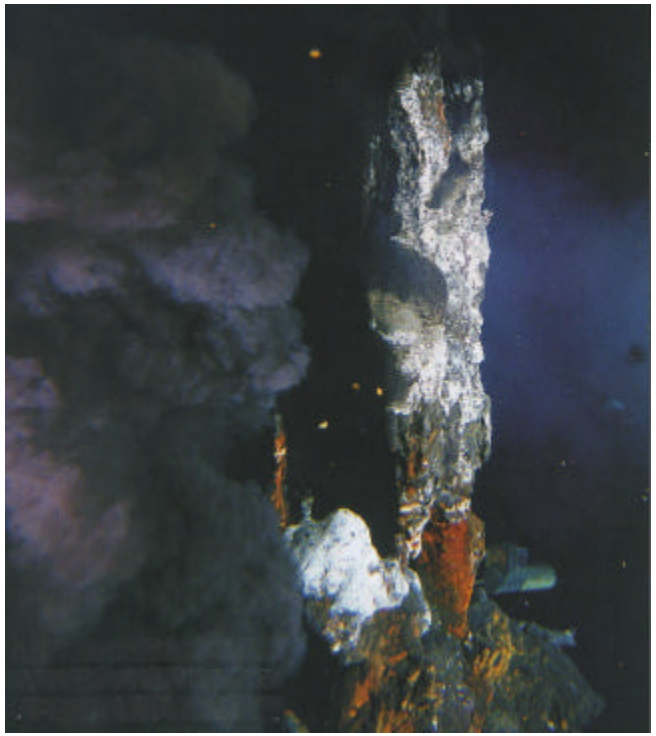
Experimental Results With PGAA

- **Comparison of certified (NIST) and measured concentrations in river sediment**

Element	CERTIFIED Concentration%	MEASURED Concentration%
Cr	2.96±0.28	≡2.96
Fe	11.3±1.2	11.5±0.3
K	1.2	1.4±0.1
Ca	2.9	3.0±0.1
Cd	0.00102±0.00009	0.00104±0.00003
Mn	0.078±0.010	0.077±0.011

Experimental Results With PGAA

- **Analysis of Deep Sea Vents (% by weight)**



	ALVIN 917-R4	ALVIN 1457-1R-C	ALVIN 1461-2R
O	45.9*	41(6), 44.9*	45.1*
S	20.0 (0.2)	0.151 (0.005)	0.16 (0.01)
Ca	11.3 (0.2)	7.22 (0.11)	7.25 (0.13)
Fe	9.28 (0.11)	9.65 (0.08)	9.37 (0.09)
Cu	7.67 (0.07)	---	---
Al	---	7.10 (0.07)	7.06 (0.12)
Mg	1.8 (0.2)	3.98 (0.11)	3.6 (0.2)
Zn	1.36 (0.05)	---	---
P	---	0.85 (0.18)	1.6 (0.2)
Ni	1.17 (0.003)	0.022 (0.002)	---
Ti	---	1.097 (0.008)	1.060 (0.010)
Si	0.55 (0.05)	22.6 (0.3)	22.3 (0.3)
H	0.368 (0.004)	0.0290 (0.0005)	0.027 (0.001)
K	0.27 (0.06)	0.138 (0.004)	0.16 (0.01)
Cl	0.194 (0.002)	0.0566 (0.0005)	0.0188 (0.0005)
Mn	---	0.154 (0.002)	0.161 (0.004)
Na	0.140 (0.014)	1.97 (0.04)	1.96 (0.05)
V	---	0.042 (0.002)	0.046 (0.003)
Co	0.0066 (0.0011)	0.0045 (0.0003)	0.0058 (0.0009)
Sc	---	0.0039 (0.0002)	0.0058 (0.0005)
Cd	0.00352 (0.00005)	---	0.00024 (0.00003)
B	0.00220 (0.00002)	0.000659 (0.000007)	0.000658 (0.000008)
Dy	---	0.00099 (0.00008)	0.00111 (0.00014)
Gd	0.000050 (0.000006)	0.000524 (0.000007)	0.000556 (0.000010)
Sm	0.00033 (0.00003)	0.000330 (0.000005)	0.000340 (0.000007)

Experimental Results With PGAA

- **Analysis of Reagent Materials**

CaF_2 (Reagent grade, Baker and Adamson)

Ca	54.3±0.9%
F	44.4±1.9%
Al	0.66±0.07%
Cl	0.150±0.003%
Na	0.040±0.009%

ZnO (Mallinckrodt)

Zn	100%)
Cd	5.1±0.3 ppm

HfO_2 (98%, Aldrich Chemical Co.)

HfO_2 (no detectable impurities)

TiO_2

Ti	96.8%
K	3.1±0.2%
H	0.04±0.01%
Eu	0.022±0.002%
Gd	5.2±0.2 ppm
B	2.0±0.2 ppm

Gd_2O_3 – no detectable impurities

$Ca(OH)_2$

Ca	93.6±1.9%
H	5.04±0.005%
K	1.3±0.2%
Cl	0.028±0.002
Eu	54±9 ppm
Gd	26±1 ppm
B	4.2±0.3 ppm

CeO_2

Ce	99.8%
K	0.077±0.016%
S	0.074±0.010%
Na	0.061±0.009%
H	0.004±0.001%
B	31±1 ppm
Eu	11±1 ppm
Sm	1.8±0.1 ppm
Gd	1.2±0.1 ppm

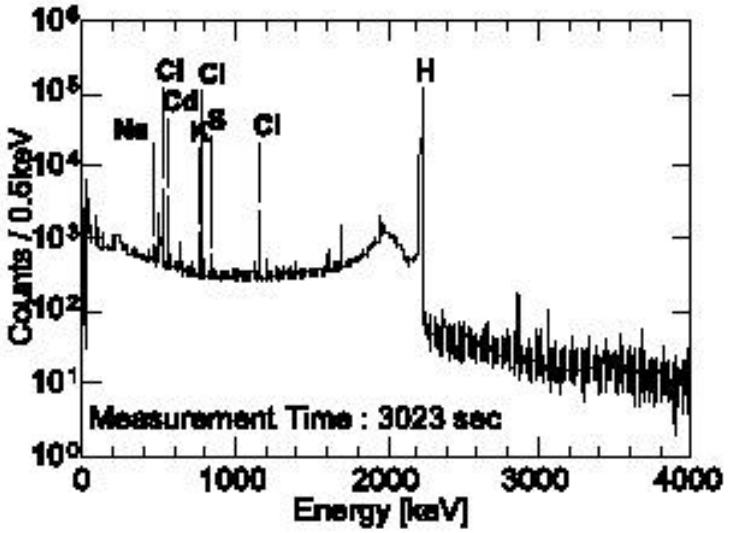


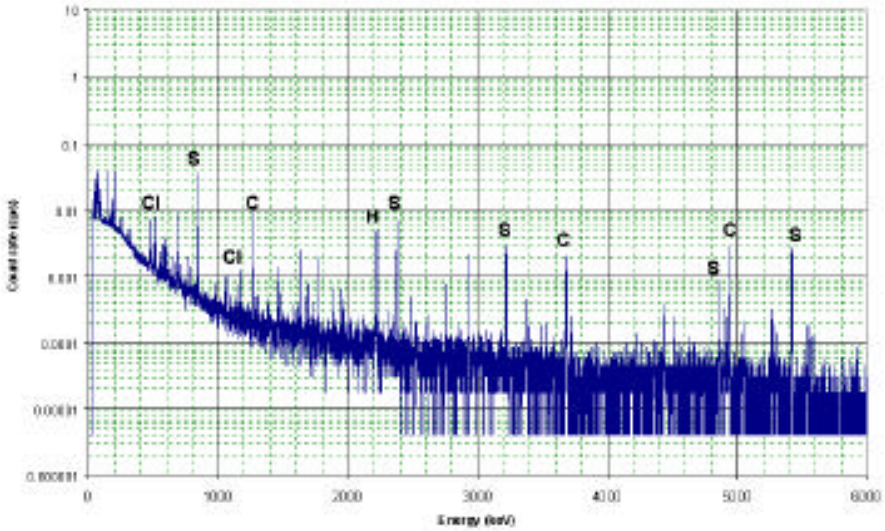
Figure 1. PGAA spectrum of 8 grams from Cd-rats 3 hrs after injection.

Table 1. Lower detection limits for PGAA

Element	Cold Neutron	Thermal Neutron
B/H	1 ppm	7 ppm
Cd/H	3 ppm	8 ppm
Hg/H	-	50 ppm
Cl/H	0.02%	0.09%
K/H	0.2%	0.5%
Na/H	0.1%	0.3%
S/H	0.4%	0.7%

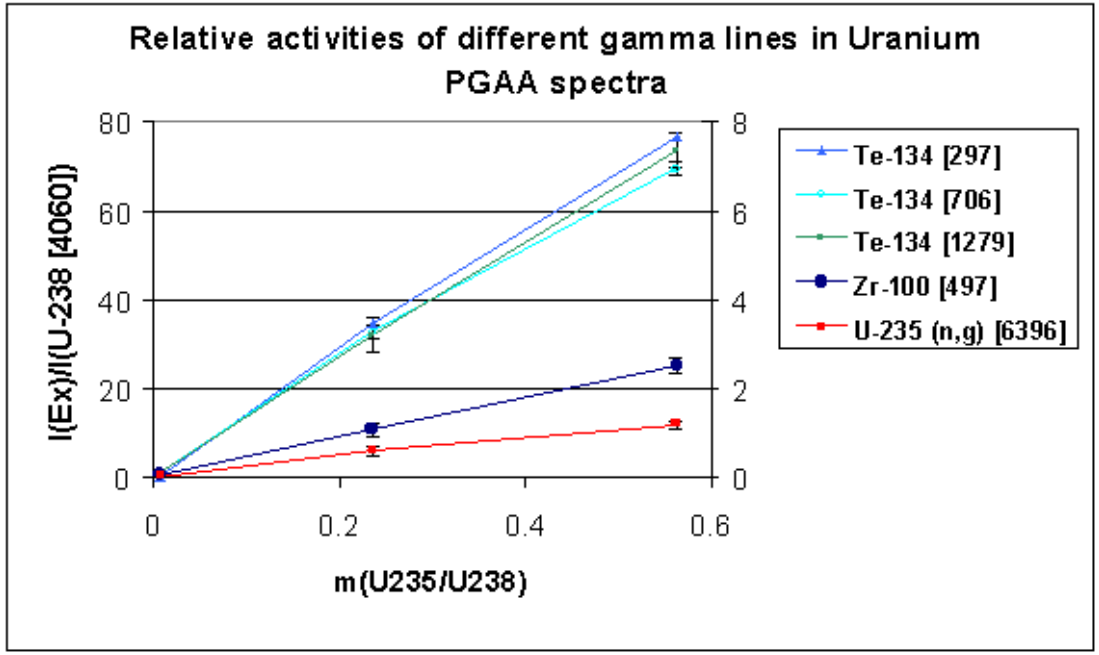
2 g of kidney irradiated with cold neutrons (1.1×10^8 n/cm^{2}s) for 50 min and with thermal neutrons (2.4×10^7 n/cm^{2}s) for 100 min. Detection limit defined as 3σ of background. (Y. Oura, S. Enomoto, and H. Nakahara, RIKEN Review **35**, 73 (2001).)

PGAA Spectrum of fullerene



Impurity content of C_{60} fullerene

Element	Conc.(%)	Unc.(%)	Composition
H	0.012	10	0.08
C	97.1	4.5	60
S	2.88	1.3	0.67
Cl	0.003	20	0.0006



Analysis of $^{235}U/^{238}U$ ratios using PGAA. Natural uranium and samples enriched to 19.1% and 36% in ^{235}U were analyzed.

Focused Beams with Cold Neutrons

Polycapillary neutron lens (NIST). 1763 glass fibres (0.5 mm), each with 1657 channels (9 μm) focus neutrons to 0.5 mm spot.